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Final Report

Field Demonstration of a Membrane Process to Separate Nitrogen from Natural Gas

Submitted by:
Membrane Technology and Research, Inc.
1360 Willow Road, Suite 103
Menlo Park, CA 94025

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National Energy Technology Laboratory

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Office of Fossil Energy

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

One West Third Street, Suite 1400
Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

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Contact: Dr. Kaaeid Lokhandwala
Tel: (650) 328-2228 ext. 140
e-mail: kaaeid@mtrinc.com

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Submitting Organization: Membrane Technology and Research, Inc.
1360 Willow Road, Suite 103
Menlo Park, CA 94025

Tel: (650) 328-2228
Fax: (650) 328-6580
www.mtrinc.com

Subcontractors: None

Other Partners: ABB Lummus Global

Project Team: Project Officer: Traci Rodosta
Contract Specialist: Keith L. Carrington

MTR Contributors to this Project: R. Baker
T. Hofmann
A. Jariwala
K.A. Lokhandwala (P.I.)
Membrane Group
Module Group
Systems Group

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Abstract

The original proposal described the construction and operation of a 1 MMscfd treatment system to be operated at a Butcher Energy gas field in Ohio. The gas produced at this field contained 17% nitrogen. During pre-commissioning of the project, a series of well tests showed that the amount of gas in the field was significantly smaller than expected and that the nitrogen content of the wells was very high (25 to 30%). After evaluating the revised cost of the project, Butcher Energy decided that the plant would not be economical and withdrew from the project.

Since that time, Membrane Technology and Research, Inc. (MTR) has signed a marketing and sales partnership with ABB Lummus Global, a large multinational corporation. MTR is working with the company's Randall Gas Technology group, a supplier of equipment and processing technology to the natural gas industry. Randall's engineering group found a new site for the project at a North Texas Exploration (NTE) gas processing plant, which met with limited success. However, a small test system was installed at a Twin Bottoms Energy well in Kentucky. This unit operated successfully for six months, and demonstrated the technology's reliability on a small scale. MTR then located an alternative test site with much larger gas flow rates and signed a contract with Towne Exploration in the third quarter of 2006, for a demonstration plant in Rio Vista, California, to be run through May 2007. The demonstration for Towne has already resulted in the sale of two commercial skids to the company; both units will be delivered by the end of 2007. Total sales of nitrogen/natural gas membrane separation units from the partnership with ABB are now approaching \$4.0 million.

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1. INTRODUCTION

The U.S. natural gas pipeline specification for inert gases is less than 4%. On this basis, about 17% of known U.S. reserves of gas are sub-quality due to high nitrogen content. Most of this gas can be brought to pipeline specifications by dilution with low-nitrogen-content gas; some is treated by cryogenic condensation and fractionation. Nonetheless, about one trillion standard cubic feet (scf) of known reserves are currently shut in. This project covers the first demonstration of a new membrane technology to treat this otherwise unusable gas.

2. EXECUTIVE SUMMARY

The general objective of this project was to develop a membrane separation process to separate nitrogen from high-nitrogen-content natural gas. Specifically, the project focused on completing a successful field test of a membrane process to upgrade nitrogen-rich natural gas to pipeline specifications (<4% nitrogen).

A proof-of-concept plant was built for a North Texas Exploration (NTE) gas field in Texas. A short test of the unit was of limited success due to a smaller-than-anticipated feed stream at the test site. A second small test system was then installed at a Twin Bottoms Energy gas well at Louisa, Kentucky. This test system worked well; after operating the test unit for six months, the well operator purchased a commercial system. Some time later, a neighboring gas producer installed a similar system. After these successful small tests, MTR located an alternative testing opportunity and ran a successful larger demonstration with Towne Exploration at Rio Vista, California, from September 2006 to May 2007. A photograph of the Rio Vista system is shown in Figure 1.



Figure 1. Skid-mounted nitrogen-separation membrane unit currently operating at a gas field demonstration site in Rio Vista, California.

The Towne Exploration test system was designed to be adjustable to accommodate variations in feed gas flow and composition. Results from the demonstration indicate that the system can handle large variations in inlet gas composition, from 8 mol% nitrogen to 16 mol% nitrogen, and still deliver gas

that meets the product gas specification of 990 Btu/scf required for delivery to the local natural gas pipeline. Based on the successful test results, Towne ordered two 10 MMscfd commercial systems in late 2006.

During the early stages of the project, MTR formed a joint development, marketing and sales agreement with the Randall Gas Technologies Division of ABB Lummus Global (ABB Lummus) to commercialize natural gas applications of membranes, including nitrogen separation. During the time while the MTR/ABB Lummus team worked on locating appropriate industry operating partners and building the project demonstration unit, other companies began to inquire about semi-commercial and commercial installations of the technology. MTR and ABB Lummus have now sold a total of eight commercial nitrogen/natural gas membrane separation units related to the technology developed during this project with total sales value of \$4.0 million.

A summary of major activities with industry partners and customers throughout the progress of the project is provided in Table 1.

Table 1. Summary of Major Project-Related Activities with End-User Partners and Customers, 2001-2007.

Partner/Customer	Date of Activity	Unit Description	Experience Gained/ Customer Status
Butcher Energy Ohio, USA	2000-2001	MTR had worked with Butcher on a small demo from a previous project. Initial intent was to scale up the same process to full commercial operation for this project.	Butcher informed MTR at the pre-commissioning meeting that flows were lower and N ₂ content was higher than anticipated in the S. Ohio field scheduled for demo unit installation. After MTR prepared new design and cost estimates, Butcher and MTR agreed that MTR should select another partner.
Omaha Public Power District Nebraska, USA	4Q 2002	Small low-pressure, non-wellhead unit built by MTR to remove N ₂ from fuel to a fuel cell.	Unit effectively reduced N ₂ content of feed stream from 6.5% N ₂ to 2.3% N ₂ at pressure of 50 psig and flow rate of 0.2 MMscfd. Unit has been in continuous operation since installation.
North Texas Exploration (NTE) Green Ranch, Texas, USA	3Q 2003- 1Q 2005	Demo unit designed for 1 MMscfd, with N ₂ content going from 24% in feed to 4% in product.	Fabricated with ABB Lummus, as part of a joint development agreement signed with MTR in 3Q 2002. Unit installed in 2Q 2004; NTE only able to produce about 0.6 MMscfd from a field that was essentially flooded with water. After several attempts to stabilize the field, the operation was stopped in early 2005, and the skid was moved from the site to a storage area in Houston, where it remains.
Twin Bottoms Energy Louisa, Kentucky USA	2Q 2004 – 4Q 2004	MTR installs a small semi-commercial demo unit to bring N ₂ from ~5.7 to 3.7% for a 0.05 MMscfd stream. Small (0.4 MMscfd) commercial unit ordered to bring gas from about 7-8% N ₂ content to 3.8% N ₂ .	Customer leased the semi-commercial unit for 6 months; unit produced pipeline-quality gas from second day of operation. Commercial unit made by MTR came on-stream in 4Q 2004 with no problems. N ₂ -content “dial-in” feature is working well.
Interstate Energy Kentucky, USA	1Q 2005- 1Q 2006	Customer with field near Louisa, KY, orders unit identical to Twin Bottoms commercial unit.	Unit shipped to site in 1Q 2006. Sale due to success of the Twin Bottoms unit.
Syntroleum For site in Kansas, USA	4Q 2005	Commercial unit ordered for flow rate of 4 MMscfd, to bring gas from 40% to 15% N ₂ at 600 psi and 4.5 MMscfd flow rate.	Unit, built by MTR, was first commercial unit from MTR to use 12-inch diameter module elements. Delivery is pending resolution of internal customer issues.
Hiland Partners For two sites in North Dakota, USA	1Q 2006 – 3Q 2006	Two commercial units ordered to bring N ₂ from 60% to 30%. Design flow rate was 4 MMscfd at 550 psig.	Both units shipped to Hiland in 3Q 2006. Unit uses 12-inch diameter module elements.
Towne Exploration Rio Vista, California, USA	2Q 2006- date	Contract signed to run demo unit on lease from 9/06-5/07. Unit brings inlet gas with 9.5-17% N ₂ (inlet Btu value of 905-960 Btu/scf) to 7.5-8.0% N ₂ product gas (product Btu value of 990 Btu/scf). Two commercial units ordered in late 2006. Maximum flow rate is 10 MMscfd at pressure of 950 psig for each unit. N ₂ removal similar to demo.	Demo unit supplied by MTR houses 3 12-inch and 3 8-inch diameter elements to process ~2 MMscfd of gas. Unit operated virtually continuously for the lease period. System can handle full range of design inlet composition to produce pipeline-spec gas. First commercial unit delivered in 2Q 2007, with second scheduled for 4Q 2007. These skids represent the largest membrane area MTR has sold for a single order.
First National Bank (Omaha) Nebraska, USA	2Q 2006 – 4Q 2006	Small unit similar to OPPD unit ordered to reduce N ₂ content from 3.8% to 1.75% for a 0.6 MMscfd natural gas stream at 40 psig.	Flawless operation since 4Q 2006 installation.
Natural gas producer Kentucky, USA	1Q 2007 - date	5.0 MMscfd unit to take 7% inlet N ₂ to product N ₂ of 3%.	Scheduled for 4Q 2007 delivery.

3. EXPERIMENTAL ACTIVITIES AND RESULTS

Technology Background

Membrane and Module Preparation

For a variety of reasons, membranes used to separate nitrogen from natural gas typically require the use of composite membrane structures. First of all, the optimum materials for methane-permeable membranes are made of rubbery polymers that are not mechanically strong. Furthermore, to obtain high permeation rates, the selective membrane must be very thin, typically between 0.5 and 5.0 μm thick. Finally, the membrane must be able to comfortably support a pressure differential of 500 to 1,500 psi. These contradictory needs are met by forming multi-layer, composite membranes of the type shown in Figure 2. The nonwoven polyester paper provides the mechanical strength required. The surface of the nonwoven is too coarse and porous to be directly coated with the ultra thin selective layer, so the paper is first coated with a microporous polymer layer. The surface of this microporous layer has pores 0.01 to 0.1 μm in diameter, so these pores are easily bridged when they are coated with the thin selective layer.

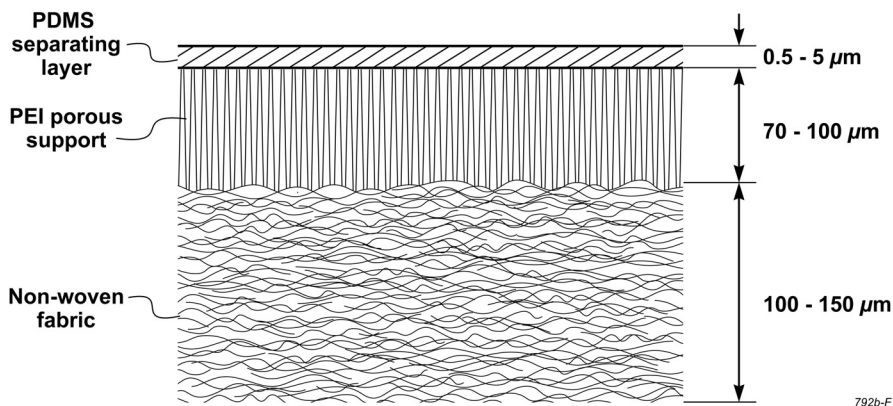


Figure 2. Composite membrane structure used to separate nitrogen from natural gas.

To meet the specific requirements of the applications in this project, a silicone rubber/polyetherimide(PEI) composite membrane structure was used; a modification in the PEI support was developed to reduce an initial problem with sheet curling, which caused difficulties in the module manufacturing process.

Even though membranes of the type shown in Figure 2 have extremely thin selective layers, many square meters of membrane are required to separate a useful amount of gas. The units into which large areas of membrane are packaged are called membrane modules. In this nitrogen separation process, spiral-wound membrane modules of the type illustrated in Figure 3 were used.

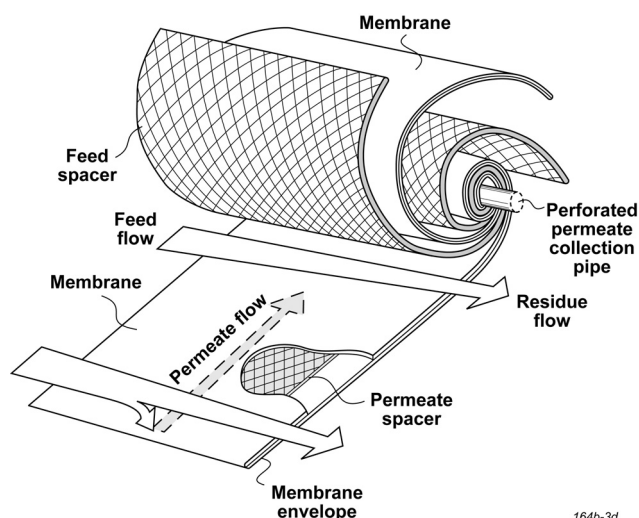


Figure 3. Schematic representation of spiral-wound membrane modules used in this project.

The wound module is contained in a tubular pressure vessel. High pressure, nitrogen-contaminated gas passes across the membrane surface. Methane and other hydrocarbons preferentially permeate the membrane, producing nitrogen-depleted permeate. The residue gas is enriched in nitrogen.

Spiral-wound modules are manufactured on an industrial scale in standardized sizes of eight-inch and twelve-inch diameter modules. A complete nitrogen/methane separation plant may use from ten to several hundred modules, depending on the size of the gas stream to be treated.

Selection of Membrane Materials^[1]

The ability of a membrane to permeate gases is measured by its permeability, P , defined as the rate that a gas permeates a membrane ($\text{cm}^3(\text{STP})\text{cm}^2\cdot\text{s}$) of standard thickness (1 cm) under a standard driving force (a pressure differential of 1 cmHg). Permeability of gases is most commonly measured in Barrer, defined as $10^{-10} \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ and named after R.M. Barrer, a pioneer in gas permeability measurements.

The membranes used industrially to separate gases are dense polymeric films that contain no pores. The permeating gas molecules dissolve in the polymer film as in a liquid and then diffuse through the membrane down a gradient in concentration created by the pressure difference across the membrane. Gas permeabilities, P , can be expressed as the product of two terms

$$P = D_i K_i \quad (1)$$

The diffusion coefficient, D_i , reflects the mobility of the individual molecules in the membrane material; the gas sorption coefficient, K_i , reflects the number of molecules dissolved in the material.

The most basic factor determining the ability of a membrane to separate two gases, i and j , can be expressed as the ratio of the gas permeabilities, α_{ij} , called the membrane selectivity

$$\alpha_{ij} = [D_i/D_j][K_i/K_j] \quad (2)$$

The ratio D_i/D_j is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio K_i/K_j is the ratio of the sorption coefficients of the two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of the two gases.

In all polymer materials, the diffusion coefficient of a gas decreases with increasing molecular size, because large molecules interact with more segments of the polymer chain than do small molecules. Hence, the mobility selectivity always favors the passage of small molecules over large ones. Another important factor affecting overall membrane selectivity is the sorption or solubility selectivity. The sorption coefficient of gases and vapors, which is a measure of the energy required for the permeant to be sorbed by the polymer, increases with increasing condensability of the permeant. This dependence on condensability means that the sorption coefficient also increases with molecular diameter because large molecules are normally more condensable than smaller ones.

In the case of high-nitrogen-content natural gas, nitrogen is smaller but less condensable than methane, so membranes can be made that preferentially permeate *nitrogen* by relying on the mobility selectivity term or that preferentially permeate *methane* by relying on the solubility selectivity term.

For this application, MTR chose to use hydrophobic rubbery polymers that permeate methane and reject nitrogen. These polymers have small diffusion selectivity terms and solubility selectivity terms close to the theoretical maximum (6 to 7). The overall selectivity of the membranes produced from these polymers (methane permeance/nitrogen permeance) is about three to four in the temperature range used in the field. Some data obtained in the laboratory and then at a pilot plant installed at a Butcher Energy gas field in Ohio are shown in Figure 4. Membrane selectivity increases at lower temperatures because of changes in the relative solubility of methane and nitrogen.

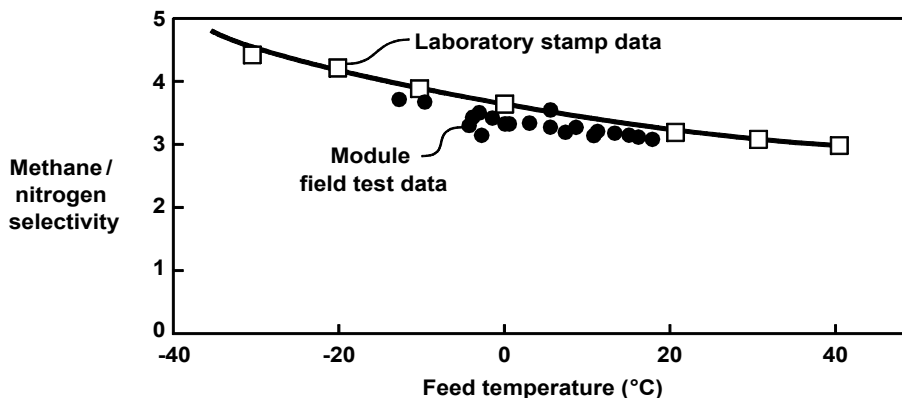


Figure 4. Comparison of laboratory and field test data for methane/nitrogen selectivity of MTR membranes used in this project.

Process Design and Economics

The main objective of this project was to complete a successful field test of a membrane process to upgrade nitrogen-rich natural gas to pipeline specifications ($<4\%$ nitrogen). The process divides the gas into two streams. The first stream is product gas containing less than 4% nitrogen, which is sent to the pipeline; the second stream, which contains $30\text{--}50\%$ nitrogen, is used to fuel the compressor engines. In some cases, a third stream is produced; this stream, which contains $60\text{--}85\%$ nitrogen, is flared or reinjected (see Figure 5).

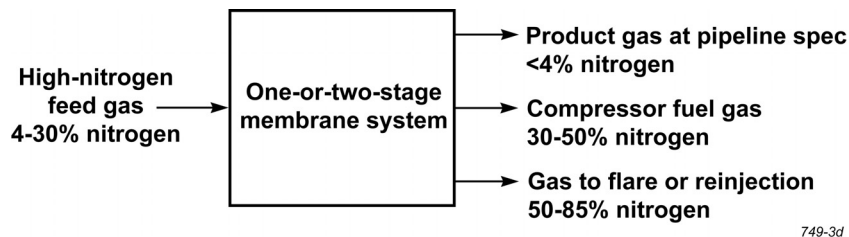


Figure 5. Block diagram of major gas stream flows in membrane separation of high-nitrogen-content natural gas.

The process, now trade-named NitroSep™, uses membranes that selectively permeate methane, ethane, and higher hydrocarbons but retain nitrogen. The design of the process depends on the concentration and the pressure of the gas to be treated and the specification for the product gas. A simple one-stage membrane unit can be used if the gas is only slightly out of spec (that is, if the gas contains $6\text{--}8\%$ nitrogen). More commonly, a two-step or two-stage membrane system is required.

NitroSep™ can be used as a stand-alone operation to process gas from as low as 0.5 MMscfd to $20\text{--}30$ MMscfd or higher. The membranes operate near ambient temperatures, and in most cases no separate dehydration or hydrate control is required. There is no accumulated liquid in the system, so there is no risk of pool fires or need to dispose of or store liquids. If desired, however, the system design does offer the flexibility to recover hydrocarbon liquids to increase total revenues.

The membrane unit is simple to operate and control. The system can reach steady state performance within minutes of startup, and can be fully automated and remotely monitored.

Over the duration of this project, MTR has designed systems capable of treating feed streams with nitrogen content varying from 4% to 30% and higher. The complexity and cost of the methane/nitrogen membrane separation process increases with the nitrogen content of the gas, especially if the product gas from the separation is targeted to contain a low mol% nitrogen. Flow schemes that summarize the major differences in process design and product stream compositions required to treat this range of nitrogen content are shown in Figures 6-8. The flow schemes are all designed for flow rates of 10 MMscfd producing a product stream containing $\leq 4\%$ nitrogen.

Treating streams with 4-8% nitrogen (Figure 6). If the feed gas contains 4-8 mol% nitrogen, a simple two-step bank of modules can be used to produce the separation required, as shown in Figure 6. Pressurized feed gas passes across the surface of the membrane: the permeate, depleted in nitrogen, is re-pressurized while the residue is used as fuel. The process achieves higher than 85% methane recovery in the product gas and even higher Btu recovery since the membrane permeates essentially all of the ethane, propane and higher hydrocarbons from the feed and residue gases. The product gas consists of nitrogen, methane, any higher hydrocarbons present, and very little else.

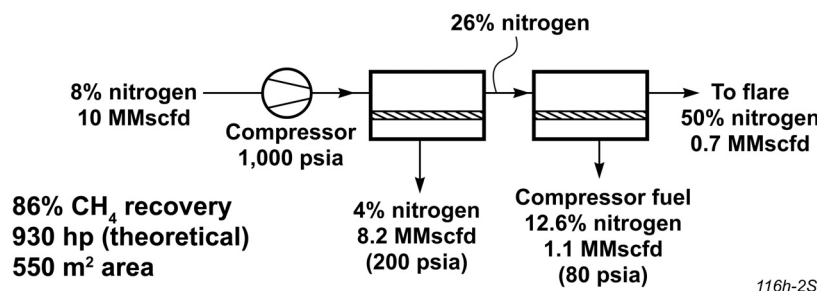


Figure 6. Flow scheme of a membrane unit that will bring natural gas with 4-8 mol% N₂ content to pipeline specification ($\leq 4\%$ N₂) using membrane-based separations. Example assumes 8% nitrogen in the gas feed.

MTR's first non-wellhead proof-of-concept system for this process was designed to treat this type of gas. The gas was being used to power a fuel cell, but contained up to 6-8% nitrogen. High nitrogen content was a problem because it produced small amounts of ammonia in the fuel cell reformer, which then degraded the fuel cell electrolyte. The customer purchased the membrane unit to reduce the nitrogen concentration to 3% in the permeate. The high-nitrogen residue gas was used as boiler fuel. This simple system has been in operation for two years and has demonstrated the overall reliability of the membranes. See discussion below on Omaha Public Power District for additional details and a photo.

Treating streams with 8-15% nitrogen (Figure 7). If the natural gas stream being treated contains more than approximately 8% nitrogen, it is no longer possible (with today's membranes) to produce gas with $\leq 4\%$ nitrogen and good hydrocarbon recovery in the product gas in a single-stage membrane process. For feed gas containing 8-15% nitrogen, the type of design shown in Figure 7 can be used. As in the Figure 6 design, the gas is passed across the first set of membrane modules to produce a permeate product gas containing $\leq 4\%$ nitrogen. The nitrogen-rich residue then passes to a second set of modules to recover additional methane.* The second membrane step residue gas will contain 25-50% nitrogen and the permeate stream will contain 6-10% nitrogen. The second-step permeate gas contains too much nitrogen to be mixed with the product gas, so it is recycled and mixed with the incoming feed gas. The residue stream containing 25-50% nitrogen gas can be used directly as compressor fuel, or treated with a third membrane to enrich the Btu value of the

* A system contains a second membrane step when the second membrane unit is placed on the residue gas from the first membrane unit. The system contains a second membrane *stage* when the second membrane unit is placed on the *permeate* gas from the first membrane unit.

compressor fuel by further nitrogen removal. As for the previous approach to treatment of 4-8% nitrogen streams, the membrane process for treating 8-15% nitrogen streams achieves about 85% methane recovery in the product gas and typically close to 93-94% Btu recovery because of preferential permeation of the higher hydrocarbons.

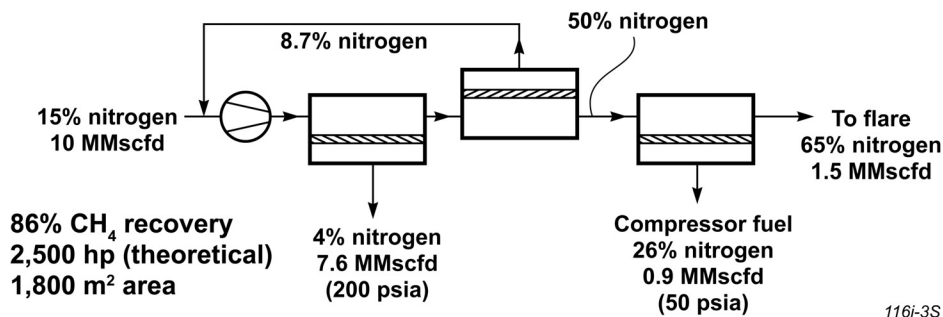


Figure 7. Flow scheme of a membrane unit that will bring natural gas with 8-15 mol% N₂ content to pipeline specification ($\leq 4\%$ N₂) using membrane-based separations. Example assumes 15% nitrogen in the gas feed.

Treating streams with 15-30% nitrogen (Figure 8). Gas containing 15-30% nitrogen can be treated by a process shown in Figure 7 or Figure 8, depending upon the product gas nitrogen-content requirements. A system with Figure 8 complexity would be required if 4% nitrogen spec for the product gas is required. The nitrogen content of the feed gas is too high for 4% nitrogen to be produced in a single membrane stage, so two membrane separation units (each with two steps) are linked. The first unit produces a residue stream containing 80% nitrogen to be flared and a low-pressure gas stream containing 11% nitrogen. This gas is fed to the second membrane unit, which produces 4% nitrogen to be sent to the pipeline and a 25% nitrogen-rich residue gas that is recirculated to the first membrane process. Compressor fuel gas is obtained by diverting a portion of the feed gas.

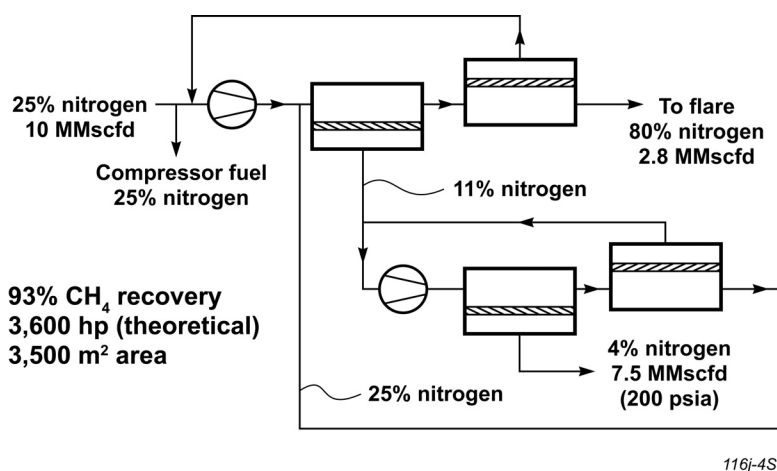


Figure 8. Flow scheme of a membrane unit that will bring natural gas with 15-30 mol% N₂ content to pipeline specification ($\leq 4\%$ N₂) using membrane-based separations. Example assumes 25% nitrogen in the gas feed.

If the gas contains more than 30% nitrogen, processing with membranes to produce pipeline quality ($\leq 4\%$) gas is usually not economically feasible. However, using the membrane process to fractionate a high nitrogen gas into a lower-nitrogen-content product gas to be diluted with low-nitrogen gas and a 70-80% nitrogen gas to be flared or re-injected can be considered (see discussion of Syntroleum Corp. and Hiland Partners in Section 3 for additional details).

All three process designs shown in Figures 6-8 recover more than 85% of the hydrocarbon values in the feed gas being treated. However, the membrane area and compressor power required for performing the separation increases sharply as the nitrogen content of the gas increases. Table 2 provides a cost summary for separation of nitrogen from natural gas for each process shown in Figures 6-8.

Table 2. Comparison of Capital and Operating Costs of the Three Nitrogen Gas Separation Systems Illustrated in Figures 6-8.

Operating Conditions and Cost Elements	Figure 6	Figure 7	Figure 8
Nitrogen concentration (%)	8	15	25
Membrane area (m ²)	550	1,800	3,550
Compressor HP (theoretical)	930	2,500	3,600
Methane recovery (%)	86	86	93
Capital Cost (Membrane Skid)	(\$1,000)	(\$1,000)	(\$1,000)
Membranes at \$200/m ²	110	360	710
Module housings (5×20m ² modules/housings at \$5,000)	30	90	155
Separators/heat exchangers/frame	100	150	200
Controls/valves	70	110	150
Flare Drier	150	150	150
Total Component Cost	460	860	1,365
Engineering/Fabrication/ Installation and Start Up at 100% of Component Cost.	460	860	1,365
Total Capital Cost	920	1,720	2,730
Annual Operating Costs			
Membrane replacement (3-year lifetime)	35	120	235
Compressor lease (\$200 hp/year)	187	500	720
Labor/maintenance at 10% of capital	92	172	273
Interest + Depreciation at 25% of capital	230	430	673
Total Operating Cost	544	1,222	1,901
Product gas (MMscfd)	8.2	7.6	7.5
Operating cost/1,000 scf of product gas (\$)	0.19	0.46	0.72

As the cost calculations in Table 2 show, the economics of the NitroSep™ process are affected by the nitrogen content in the feed gas, the value of the product gas, and the maximum allowable nitrogen content in the product gas. For up to about 30 mol% nitrogen in the feed, the membrane

process can provide a solution that is economically feasible. The membrane process is especially suited to processing smaller flow rates of gas, allowing smaller wells to be produced economically. The membrane process is flexible and can be designed to maximize hydrocarbon utilization and revenues. The Btu value of the nitrogen-reject stream can be tailored to match the fuel specification of compression sets used in the NitroSep™ process, or can be used to produce electric power in a generator set-up (gen set) for electrically driven compressors. In addition, virtually all ethane and heavier components are recovered in the product gas sent to the pipeline. This maximizes the Btu value of the product stream, thereby increasing the total generated revenues. The overall membrane process can be designed to recover not only pipeline-spec natural gas, but also NGL, as a separate product. In addition, if required, the overall process (including a gen set) can provide electrical power for sale to the grid.

Project Activities and Results by Company

Over the course of this project, MTR provided demonstration and/or commercial units to ten different companies. A summary of major project-specific activities is provided in Table 1 of the Executive Summary. The activities and results are discussed by company for each of MTR's partners and customers in the sections that follow.

Butcher Energy Corporation

At the beginning of this work, Butcher Energy Corporation was MTR's project partner. MTR had successfully operated a small demonstration of the proposed process at a field operated by Butcher on a previous project. The first pilot-scale field trial of nitrogen separation from natural gas was conducted on a shut-in gas well with gas containing 15% nitrogen, and was delivered to the module test unit at a pressure of 900 psi. The objective of this test was to evaluate the long-term performance and stability of membranes when tested with raw filtered, but otherwise untreated gas.

The field test system was made by modifying an existing system. Figure 9 shows a simplified flow schematic of the unit. The system contains two filter separators, one at the front end for particulate matter and another coalescing filter for condensate and natural gas liquids. Following the first filtration, the feed gas enters a set of three membrane modules (3-inch diameter), which dehumidify the gas stream. The dried gas enters the heat exchangers which pre-cool the stream; any condensed liquids are separated in the coalescing filter before the gas enters the membrane unit. The methane-enriched gas is removed as a low-pressure permeate, and the non-permeate nitrogen-enriched gas is removed as a residue gas. Both the permeate and residue gases from the membrane system are 20-30°C colder than the inlet gas because of Joule-Thompson expansion that occurs as the high-pressure feed gas permeates through the membrane to the low-pressure permeate side. In addition, the high-pressure, nitrogen-enriched residue gas is expanded through a Joule-Thompson valve to achieve further cooling. Both the permeate and residue gas streams are used in the heat exchangers to cool the incoming feed stream. (Calculations showed that the temperature of the test module could be lowered to -20 to -40°C by using Joule-Thompson cooling; however, in field operation, because of heat losses in the system, the lowest incoming temperature of the gas to the module was only (-5) to (-10)°C. Consequently, the heat exchangers were added to the design.)

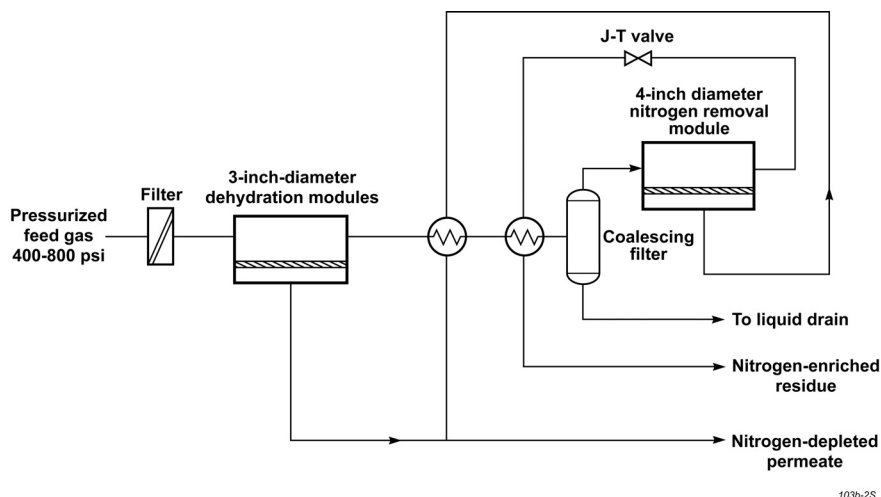


Figure 9. Simplified flow schematic of the membrane pilot-scale field test unit.

The system was operated at a Butcher Energy gas well in Southern Ohio for more than one year. Some typical results were shown previously in Figure 4; they are repeated for convenience in Figure 10. The module performance was essentially identical to that of membrane stamps tested in the laboratory. After six months' operation, the first membrane module was removed for examination; its permeation properties were unchanged from those measured prior to the field test. Based on these results, membrane lifetimes in this application were estimated at 3 to 5 years, similar to those obtained with other similar gas separation membranes used in petrochemical plants.

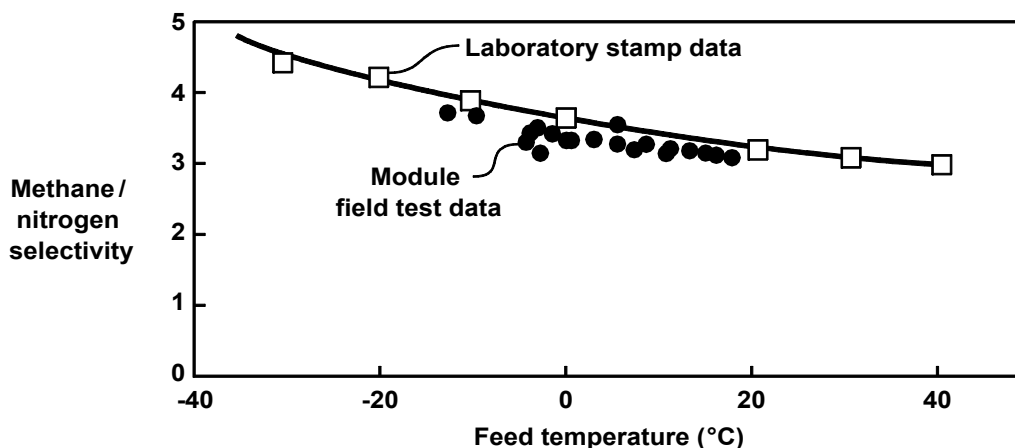


Figure 10. Methane/nitrogen selectivity as a function of gas temperature in laboratory membrane stamp tests and module test performed over a six-month period at Butcher Energy's Ohio gas field.

Work from the pilot-scale test led to this project for a full commercial demonstration of nitrogen separation from high-nitrogen content natural gas. MTR expected to build and install a 1 MMscfd membrane treatment system to treat gas containing just over 15% nitrogen at one of Butcher Energy's high-nitrogen gas fields in Jackson County, Southern Ohio.

During pre-commissioning of the project in late 2001, a series of well tests showed that the amount of gas in the field was significantly smaller than expected and that the nitrogen content of the wells was very high (25 to 30%). After evaluating the revised cost of the project, Butcher Energy decided that the plant would not be economical and withdrew from the project. MTR and Butcher agreed that MTR would be free to select another partner for this project.

Joint Development Partnership Formed: ABB Lummus Global – Randall Gas Technology Group

In mid-2002, MTR signed a joint development, marketing and sales partnership with the Randall Gas Technology Group of ABB Lummus Global (referred to as ABB Lummus following this paragraph) to encourage more rapid development of several membrane technologies suitable for application in the natural gas industry, including the nitrogen separation applications developed in this project. ABB Lummus Global is a large multinational corporation with a strong reputation in process engineering and construction; Randall has a similar reputation as a supplier of equipment and processing technology to the natural gas industry.

After a number of false starts at locating a field site for the technology, ABB Lummus identified a site at a North Texas Exploration (NTE) gas processing plant in Green Ranch, Texas. ABB Lummus and MTR worked closely together and with NTE on the demo unit, as described in the next section.

North Texas Exploration (NTE) Demonstration Unit

NTE was selected by ABB Lummus as a viable candidate for a demonstration unit that would separate nitrogen from natural gas at a small high-nitrogen gas field in Green Ranch, Texas. Nitrogen content of the well gas was 20-25%, going to 4% nitrogen in the product gas. NTE was looking for an economical and easily expanded nitrogen removal unit that could operate unattended at a remote site. Feed flow rate was expected to be about 1 MMscfd.

MTR and ABB Lummus designed and built a system for NTE based on the flow scheme provided in Figure 11. Skid design including piping and instrumentation diagrams (P&IDs) was completed in mid-2003, and fabrication was completed in January 2004. Figure 12 provides a photo of the membrane skid just prior to shipment to the NTE pilot test.

MTR fabricated an initial set of thirty-four eight-inch-diameter spiral-wound modules in late 2003 for the NTE demonstration (see Figure 3 for a schematic diagram of the module structure). Each module contained about sixteen square meters of membrane. QA/QC tests were performed with satisfactory results. In early 2004, the modules were loaded into the demonstration system and the membrane skid was installed. The unit started up at the NTE site in the second quarter of 2004. Pictures taken during installation of the unit are shown in Figures 13 and 14.

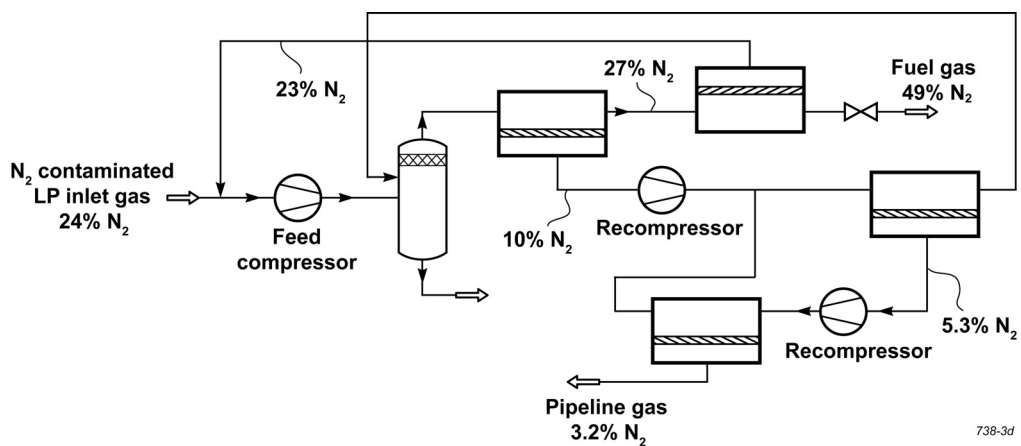


Figure 11. Process flow diagram for the NTE pilot plant system. Nitrogen content of the well gas was 20-25%, going to $\leq 4\%$ nitrogen in the product gas. Feed flow rate of the design was 1 MMscfd.



Figure 12. Photo of demonstration skid ready for shipment to NTE pilot test site.



Figure 13. Membrane system being installed for NTE at Green Ranch, Texas.



Figure 14. Membrane system being installed for NTE at Green Ranch, Texas.

The system was able to produce a pipeline-spec product gas and a 50% nitrogen fuel gas that powered the unit's compressors, and was built to accommodate changes in the nitrogen content and volume of raw gas. Unfortunately, NTE's problems with the quantity of well output and water content at the selected site kept this unit from being operated for any significant length of time. The client was expecting to get a minimum of 1 MMscfd of inlet gas, but had been able to produce only about 0.6 MMscfd. The inlet gas was water saturated and this caused problems during compression. The compression equipment was adjusted to operate in a stable range, with the unit operating at 50%

capacity in late 2004. However, operation stopped in early 2005, and the system was removed from the site due to NTE's constant gas production issues. The unit was moved to Houston for storage, where it remains.

Omaha Public Power District (OPPD):

Fractionation of Non-Wellhead, Low-Nitrogen (4-8%) Gas

In 2002, OPPD approached MTR to see if the technology being developed for nitrogen removal from natural gas could be applied to a small, low-pressure, non-wellhead application. OPPD was operating a natural gas-powered phosphoric acid fuel cell used for non-interruptible power. The local gas supply contained up to 6.5% nitrogen. When processed by the fuel cell reformer, the nitrogen caused a small amount of ammonia to form (ppm levels). Over time, this small amount of ammonia degraded the performance of the fuel cell; reducing the nitrogen level of the gas to below 2.5% nitrogen was required to solve the problem.

A flow diagram and photograph of the system installed to meet OPPD's requirements are shown in Figures 15 and 16. The feed gas pressure was very low (only 50 psia), so the pressure difference across the membrane was quite small. Even so, the OPPD unit has been in operation since 2002, producing about 2.3% nitrogen gas. The residue gas containing about 15% nitrogen is used as boiler fuel.

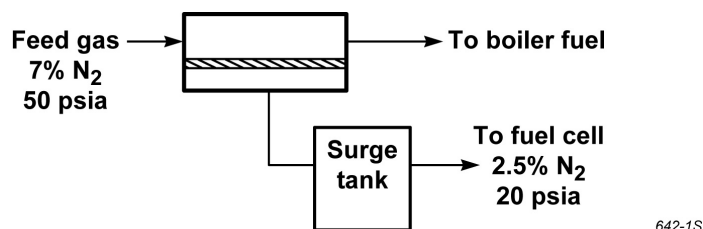


Figure 15. Flow schematic for a one-step membrane unit to lower nitrogen content of natural gas from 7% to 2.5%. The boiler fuel contains about 15% nitrogen.



Figure 16. A simple one-stage membrane unit to produce low-nitrogen natural gas for phosphoric acid fuel cells.

***Twin Bottoms Energy and Interstate Energy:
Wellhead Fractionation of Gas with 4-8% Nitrogen***

The nitrogen/natural gas separation system shown in Figures 13 and 14 was operated on gas that met all normal pipeline specifications, except that the local pipeline gas supply contained up to 6-8% nitrogen. The first system to lower the nitrogen content of a raw field gas feed was constructed in 2004, concurrently with the NTE demonstration unit. In the fuel cell application, the overall hydrocarbon recovery was only ~50%; this was acceptable because the high-nitrogen gas by-product was used as boiler fuel. Gas processors require much higher hydrocarbon recoveries since the high-nitrogen gas residue produced is a waste stream. Some of the high-nitrogen gas can be used as fuel, but the remainder is often just vented. Hydrocarbon recoveries of 80-90% are needed. For this reason, two-step units of the type shown in Figure 6 are used.

Two small two-step systems were installed in Kentucky, where gas containing 6 to 15 % nitrogen is common. For one of these units, the incoming low-pressure feed gas contained about 7% nitrogen. After compression to 310 psia, the gas was passed through two sets of modules in series. The permeate from the first step contained 3.8% nitrogen. The residue gas containing 11.8% nitrogen was sent to a second step where it was converted to 17-20% nitrogen. This gas was used as fuel for the compressor. The permeate from the second step containing 6 to 7% nitrogen was recirculated to the inlet of the feed compressor. The system achieves 80 to 85% hydrocarbon recovery in the product gas.

A photograph of the unit installed at Louisa, Kentucky, for Twin Bottoms Energy, similar to the system installed for Interstate Energy, is provided in Figure 17. While design of the two units is nearly identical, “dial-in” features of the design developed by MTR allow each producer to vary the size of the stream and the nitrogen content of the stream being treated.



Figure 17. Photograph of a two-step membrane unit processing 0.4 MMscfd of natural gas to lower nitrogen content from 7% to 3.8% in Louisa, Kentucky. Operator is Twin Bottoms LLC. Interstate Energy operates a very similar system nearby.

**Syntroleum Corp. and Hiland Partners:
Treatment of High-Nitrogen-Content (40-60%) Gas Streams**

With high-nitrogen gas streams, containing greater than 15% nitrogen, it becomes increasingly difficult to meet pipeline specifications even with a two-stage or two-step process. Three stages can be used, but the extra compression involved and the system complexity can make the process uneconomic. Fortunately, the nitrogen specification for the product gas from membrane units used to separate high-nitrogen gases is often 10% nitrogen or even higher. If the product gas can be brought to this level of nitrogen content, it can then be diluted with low-nitrogen gas to meet the pipeline specification, or used as on-site fuel for compressors or other electrical equipment.

The process design for the Syntroleum system built to treat 40%+-nitrogen gas is shown in Figure 18. The design is similar to the general design shown previously in Figure 8 and the NTE demonstration skid design shown in Figure 11. A two-step/two-step process design (two-stage process in overall design) is used to bring the feed gas at 41% nitrogen to a high-nitrogen-content vent gas at 82% nitrogen and a product gas at 18% nitrogen. A photo of the unit is provided in Figure 19.

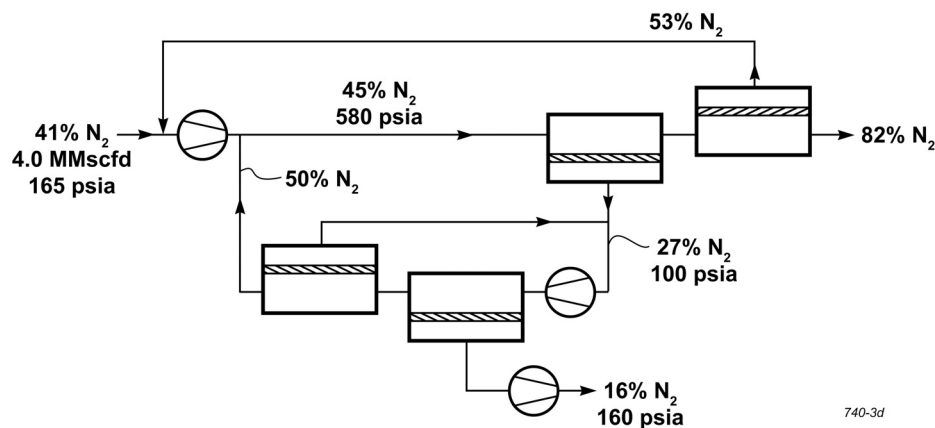


Figure 18. Flow diagram of a 4 MMscfd system built to fractionate a high-nitrogen gas stream into a 16% nitrogen stream to be diluted and sent to the pipeline and an 82% nitrogen waste stream to be vented.



Figure 19. Syntroleum system ready for installation.

The flow scheme for the Hiland Partners system is shown in Figure 20. This simple system was designed to treat associated off-gas produced in an in-situ combustion process. The off-gas contained up to 60% nitrogen and 10% CO₂. The gas had too low a Btu value to be used as fuel; however, by removing nitrogen from the gas, the Btu value could be increased from 450 Btu/scf to 875 Btu/scf. This higher Btu gas could then be used as turbine fuel.

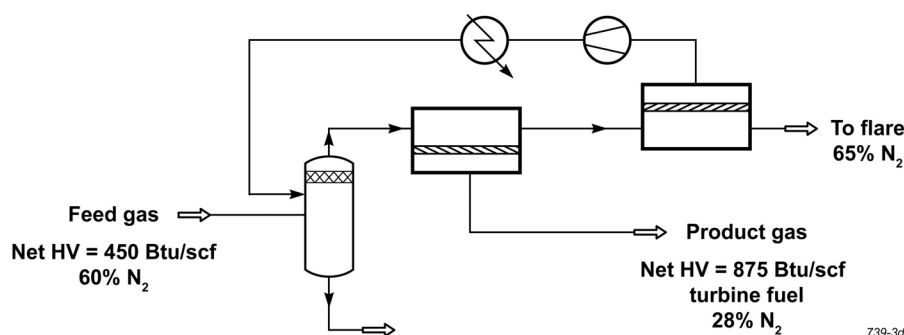


Figure 20. Flow schematic of the Hiland Partners nitrogen removal system.

New 12-inch diameter membrane modules. The Syntroleum and Hiland units were the first commercial units for which MTR provided module elements with 12-inch diameters. The 12-inch elements each contained about 50 square meters of membrane, and the 8-inch elements were each about 20 square meters. A photograph comparing the 8-inch and 12-inch modules is provided in Figure 21.

These 12-inch elements were the first ones of that size manufactured by MTR. Their successful

introduction will allow significant cost reductions on a per-square-meter-of-membrane basis for any membrane applications requiring high feed flow rates.



Figure 21. Comparison of 12-inch and 8-inch membrane modules. The 12-inch modules contain about 50 square meters of membrane, and the 8-inch modules contain about 20 square meters. The 12-inch elements made during this project were the first ones of that size manufactured by MTR. Their successful introduction will allow significant cost reductions on a per-square-meter-of-membrane basis for any membrane applications requiring high feed flow rates.

A photo of a batch of 12-inch modules prior to shipment for incorporation into a module skid is shown in Figure 22 (the gentleman in the figure is Dr. Lokhandwala, project PI).



Figure 22. Ready-to-ship batch of MTR's new high-capacity 12-inch NitroSep™ modules.

***Towne Exploration:
Demonstration Unit Leads to Commercial Sales***

Towne Exploration demonstration unit. In mid-2006, MTR signed a nine-month lease contract with Towne Exploration to run a demonstration unit at a site operated by Towne Exploration in Rio Vista, California, from September 2006 through May 2007. This was the most successful of the demonstration units for this project.

MTR supplied a test unit that housed three 12-inch membrane elements and three 8-inch elements, capable of processing about 2 MMscfd of gas containing from 9-15 mol% nitrogen. The original requirement was to reduce the nitrogen content to a level such that the gross Btu value of the product gas was at least 990 Btu/scf.

The design of the plant was a two-step process similar to that shown previously in Figure 7. The feed gas contained 16% nitrogen, and had a heating value of 900 Btu/scf. The pipeline would accept this gas for dilution with low-nitrogen gas if the heating value could be raised to 990 Btu. To reach this target, the feed gas, at a pressure of 980 psia, was passed through three sets of modules in series. The permeate from the front set of modules was preferentially enriched in methane, ethane, and the C₃₊ hydrocarbons, and the nitrogen content was reduced to 9% nitrogen. These changes raised the heating value of the gas to 990 Btu/scf. This gas was compressed and sent to the pipeline. The residue gas from the first set of modules containing 22% nitrogen was sent to a second membrane step where it was concentrated to 60% nitrogen. The permeate from the second step contained 18% nitrogen and was recycled to mix with the feed gas. The residue gas from this unit was then sent to a final small system to be fractionated. The permeate gas containing 40% nitrogen was used as fuel for the compressor engines. The final residue contained 65-70% nitrogen and was essentially stripped of all C₃₊ hydrocarbons; it was then vented.

The unit was installed with no major difficulties, and was online virtually continuously from September 2006 through June 2007. Figure 23 provides a photo of the installation and Figure 24 provides a flow diagram. The system demonstrated that it can handle large variations in inlet gas composition, from 8 mol% nitrogen to 16 mol% nitrogen, and still deliver gas that meets the pipeline product gas specification of 990 Btu/scf. During early 2007, Towne operated the Rio Vista demonstration unit continuously to treat a feed gas containing 16 mol% nitrogen. The feed gas had a Btu/scf value of 900 Btu/scf; Towne upgraded the gas to 975 Btu/scf, and delivered it (together with other streams) to a Pacific Gas & Electric (PG&E) pipeline serving the entire Northern California area.



Figure 23. Skid-mounted nitrogen-separation membrane unit operated at a gas field demonstration site in Rio Vista, California. This was the most successful of the demonstration units for this project.

This unit recovered 95% of the hydrocarbon values for delivery to the pipeline, 2% of the hydrocarbons were used as compressor fuel and the final 3% were vented with the separated nitrogen.

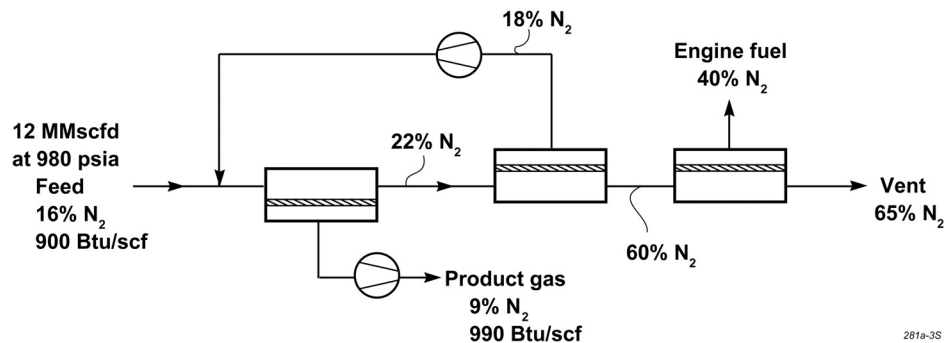


Figure 24. Flow diagram of a 0.8 MMscfd membrane nitrogen removal demonstration plant installed on a high-nitrogen gas well in the Sacramento River Delta region of California.

Field Test Results: Six-week Record of Performance

The Towne demonstration unit started operation in the third week of September 2006. Before the end of the month, real-time performance data were being generated on an hourly basis. The average daily results are summarized in Figure 25 for the first six weeks of operation. The data confirm a product gas with heating value of 990 Btu/scf was produced with good consistency early in the test

period. The days when heating value of the product gas dropped to 950-970 Btu/scf were due to compression capacity issues which were limiting the recycling of gas, affecting productivity as well as product purity. These problems were resolved by purchasing extra compressors.

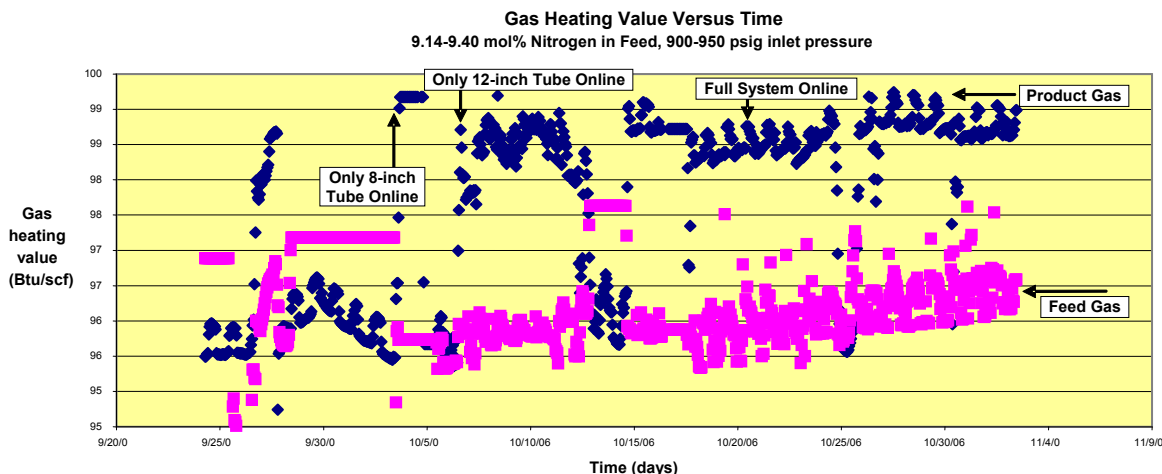


Figure 25. Daily average product gas heating value for first six weeks of demonstration unit operation at Towne Exploration in Rio Vista, California (September-November 2006).

Towne Exploration orders commercial units. The successful demonstration tests described above led Towne to purchase two commercial-scale units in late 2006. The units are designed to treat gas containing 8-16% nitrogen, to bring it to Btu-based gas specs, equivalent to nitrogen content of about 5-10% in the treated stream. The first of Towne's two identical commercial skid units was delivered in 2Q 2007, with the second scheduled for 3Q 2007. These skids represent the largest membrane units (measured in membrane area) that MTR has sold for a single order. Photographs of the first unit are provided in Figures 26-28. Data comparing actual performance to design specifications for the unit in late August are provided in Table 3.



Figure 26. Commercial unit sold to Towne Exploration for treating gas containing 8-16% nitrogen.



Figure 27. Commercial membrane system being installed at Towne Exploration site in Rio Vista, California.



Figure 28. End view of commercial membrane system installed at Towne Exploration site in Rio Vista, California.

Table 3. Comparison of Design and Actual Performance for the First of Towne Exploration's Commercial Nitrogen-Separation Membrane Units at Rio Vista, California (August 25, 2007).

	Feed Gas		Product Gas		Vent Gas		Recycle Gas	
	Design	Actual	Design	Actual	Design	Actual	Design	Actual
Btu/scf (daily average)	908.000	908.05	988	976.957	300	421.361	865	881.425
Operating Conditions								
Pressure(psig)	960.000	847.00	795.000	821.000	952.000	828.000	970.000	840.000
Temp(°F)	104	76	110	86.8	90	63	104	104
Volume(MMscfd)	2.00	1.738	1.65	1.423	0.21	0.188	5.37	2.711
Stream Compositions (daily average mol%)								
N ₂	16.054	15.34	9.060	9.292	70.028	58.883	17.161	16.335
CO ₂	0.225	0.26	0.260	0.301	0.003	0.026	0.127	0.183
Methane	78.992	80.70	85.222	86.116	29.900	40.722	79.863	80.932
Ethane	2.095	1.95	2.421	2.249	0.045	0.217	1.344	1.411
Propane	1.086	0.95	1.264	1.107	0.010	0.078	0.605	0.620
n-Butane	0.261	0.24	0.307	0.284	0.001	0.017	0.115	0.146
Isobutane	0.302	0.20	0.355	0.239	0.001	0.017	0.133	0.132
n-Pentane	0.086	0.07	0.101	0.083	0.000	0.005	0.037	0.042
Isopentane	0.201	0.08	0.237	0.097	0.000	0.006	0.084	0.050
n-Hexane	0.044	0.22	0.053	0.229	0.000	0.028	0.018	0.149
C ₆ + Hydrocarbons	0.220	0.22	0.252	0.229	0.020	0.028	0.085	0.149

First National Bank (Omaha)

In early 2006, MTR received an inquiry from First National Bank of Omaha for a unit similar to the one supplied to OPPD. The unit was installed in 4Q 2006, and has operated flawlessly since that time.

Natural Gas Producer (Kentucky)

In early 2007, another natural gas producer in Kentucky ordered a 5.0 MMscfd unit to take feed gas containing 7% nitrogen to product gas containing 3% nitrogen. The required separation is very similar to that of the previous units installed in Kentucky for Twin Bottoms and Interstate Energy, but with ten times the feed flow rate. The unit is scheduled for delivery in 4Q 2007.

4. MARKETING AND COMMERCIALIZATION ACTIVITIES

MTR and ABB Lummus have now sold commercial nitrogen/natural gas membrane separation units related to the technology developed during this project to eight customers. Commercial sales of natural gas/ nitrogen membrane separation units related to this project technology now total \$4.0 million.

- The Omaha Public Power District (OPPD) unit was MTR's first commercial nitrogen/natural gas unit, and has operated with virtually no downtime since it was installed three years ago.
- The Twin Bottoms, Kentucky, system installed in November 2004 remains in continuous operation, and is now operating at its maximum design capability.
- Interstate Gas ordered a unit like the Twin Bottoms unit in 2005, and it was shipped to the client in February 2006.
- First National Bank of Omaha ordered a unit that was shipped in February 2006, and on-site start-up and installation was completed in March. The client signed off on successful implementation and startup, and the system is in full commercial operation, delivering "stellar" performance as per the system design.
- Syntroleum Systems (Tulsa, Oklahoma) ordered a unit in late 2005. The unit is ready for installation, pending resolution of internal issues at Syntroleum.
- Hiland Partners (Dallas, Texas) ordered a unit in 4Q 2005 for a site it operates in North Dakota. This unit was delivered in June and started up in December 2006.
- Hiland ordered a second unit/skid in the first quarter of 2006, which was also delivered in June. Hiland will use its own staff for start-up of this unit.
- Towne Exploration ordered two commercial scale units in late 2006. Combined value of the two units was \$1.4 million.
- Another natural gas producer in Kentucky ordered a unit similar to the Twin Bottoms and Interstate Gas units in early 2007, but with ten times the feed flow rate. Delivery is scheduled for 4Q 2007.

Currently, there are several potential orders under review by customers (Mexico, Saudi Arabia, and Pakistan, to name a few), and inquiry activity continues at a high level.

Defining the Market

The general objective of this project was to develop a membrane separation process to separate nitrogen from high-nitrogen-content natural gas. Specifically, the project focused on completing a successful field test of a membrane process to upgrade nitrogen-rich natural gas containing 4-30% nitrogen to pipeline specifications (<4% nitrogen).

During early commercialization, MTR discovered an important potential future market for its NitroSep™ technology: bringing very-high-nitrogen-content gas streams containing as much as 40-50% nitrogen down to levels of 10-15%. This market differs from MTR's initial target of bringing all product streams to 2-4% nitrogen. Many gas producers operate with access to large gas gathering and processing networks. For this type of operator, bringing the nitrogen content of high-nitrogen wells to lower levels allows them to use the resulting product stream for blending with larger volume low-nitrogen content streams. This meant that a larger universe of gas streams could be considered for treatment using membrane-based nitrogen separation technology. In fact, two of MTR's early commercial units were purchased to bring gas containing 40-60% nitrogen down to nitrogen levels of 15-30% for blending or fuel use.

MTR also found niche applications for the technology in purification of non-wellhead natural gas containing small quantities of nitrogen, where continuous operation of a very low maintenance technology was required. Two customers are using small membrane units to bring natural gas streams from about 4-7% nitrogen to 1.75-3.8% nitrogen.

In general, MTR has learned that the NitroSep™ technology can be applied to a much broader set of applications than originally anticipated. At the same time, it became clear that many companies deal with high-nitrogen-content gas simply by dilution of such streams with higher quality streams from a variety of sources. Fortunately for membrane companies, nitrogen is difficult to economically separate from methane by any technology. This means membrane systems are the lowest cost way to treat many nitrogen-containing gas streams, when treatment is required.

Collaborating with ABB Lummus Global – Randall Gas Technologies (ABB Lummus)

During 2001 and 2002, MTR explored the possibility of cooperating with a large multinational company as a marketing and sales partner, and in September 2002, MTR signed a marketing agreement with ABB Lummus Global and its Randall Gas Technology Group, located in Houston, Texas. Randall is a world leader in supplying technology and equipment for large natural gas processing projects. In addition to providing access to Randall's marketing channels and the expertise of their process and engineering staff, partnering with ABB Lummus gave MTR a level of customer credibility that it did not have previously in the gas processing industry. The MTR-ABB Lummus relationship continues to the present time.

As part of the alliance activities, MTR and ABB Lummus have developed various strategies and tactics to address what have been identified as key requirements of customers in the natural gas and gas processing industries. In particular, MTR and the alliance have

- Developed a standardized layout and membrane skid to lower repetitive engineering costs and to develop essentially reusable systems
- Developed a detailed package of system specifications to allow rapid transfer of information to potential clients
- Built a network of fabrication shops and contacts to minimize building costs and accelerate delivery schedules

Completing all of these tasks has allowed the MTR-ABB Lummus alliance to respond quickly and efficiently to inquiries from potential customers, as well as to offer units that are well-priced in terms of payback time for the user.

Formulating a Comprehensive Commercialization Plan

Most of MTR's seven-point commercialization plan was developed in conjunction with ABB Lummus in 2004, and refined in the years since that time. Eight customers have already built and installed nitrogen/natural gas separation units for use in remote gas processing locations, and MTR continues to receive inquiries and orders from companies worldwide.

The seven points addressed in the commercialization plan included:

1. Access to markets and collection of qualified leads and prospects
2. Ability to provide a technically adequate solution
3. Customer confidence and comfort with the new technology
4. Development of a competitive and profitable pricing structure
5. Timely delivery of orders
6. Ability to predict and control costs to ensure profitability
7. Ability to provide clients with alternative financing methods, including leases and processing fees

This outline continues to serve as a framework for NitroSep™ commercialization efforts.

Marketing Via an MTR Website Presence

Separately from the collaborative agreement with ABB Lummus, MTR began marketing the new nitrogen separation technology using the MTR website at www.mtrinc.com. MTR saw immediate increases in website traffic when the natural gas products were introduced in 2001. The website approach has produced consistent results in generating high quality leads and inquiries for sales of nitrogen separation units. *All* systems sales related to this project have been developed starting from MTR website marketing efforts. An excellent example is Towne Exploration. Towne initially

contacted us via the MTR website, leading to both the field test demonstration and the purchase of commercial units. MTR continues to generate inquiries every week from the website, in addition to leads from other established marketing channels. A revised and expanded section of the MTR website, devoted to natural gas applications, is in beta testing stages, and will be rolled out by October 2007 (<http://www.mtrinc.com/Pages/NaturalGas/ng.html>).

Other Marketing Approaches: Presentations, Papers and Industry Shows

Dr. Lokhandwala of MTR presented summaries of nitrogen separation technology progress at the Gas Processors' Association (GPA) Annual Meeting in 2002,^[2] and, with an ABB Lummus co-presenter, at the Laurance Reid Gas Conditioning Conference (LRGCC) and GPA Annual Meeting in 2004.^[3,4] In 2005, Mr. Jariwala of MTR presented a paper on nitrogen-rejecting membranes at the Annual International Petroleum Environmental Conference in Houston.^[5] Mr. Jariwala recently submitted an abstract to present a paper on nitrogen separation at the upcoming GPA Annual Meeting to be held in March 2008.

Mr. Zammerilli from NETL approached MTR in 2006 about providing a paper for *GasTIPS* on the nitrogen-rejection technology being developed in this project, and worked with Dr. Lokhandwala to complete and publish the paper in late 2006.^[6] Dr. Lokhandwala also worked with Dr. Baker of MTR to prepare a review paper on use of membranes in natural gas applications for *I&EC Fundamentals*; the review was submitted in August 2007.^[7]

MTR was invited to participate in the Ohio Technology Showcase sponsored by DOE OIT in September 2005 in Cleveland, Ohio (www.ohioshowcase.org); nitrogen removal from natural gas was among the energy-efficient membrane technologies presented by MTR. MTR also participated for the first time in the biannual International Expo for oil and gas producers in Calgary, Alberta, in June 2006. The MTR booth and handout materials included several nitrogen removal case studies.

Operation of the demonstration units, especially the Towne Exploration unit, also provided MTR with some excellent opportunities to showcase the technology with prospective clients.

5. CONCLUSIONS

MTR successfully developed and demonstrated a membrane separation process, NitroSep™, to separate nitrogen from high-nitrogen-content natural gas during the execution of the project. The successful demonstration resulted in the sales of several commercial units. All installed commercial units are operating at or better than guarantee conditions and clients have given MTR several good references for further development of this business. Total commercial sales of \$4.0 million have been made for the product line developed from this project. Further sales are expected in 2007.

NitroSep™ systems can be as simple as a single stage unit, to treat streams that are only slightly out of specification in nitrogen, or can have two or more steps or stages to achieve high hydrocarbon recovery and nitrogen levels less than 2%. The flexibility of the membrane system allows for significant variations in inlet gas compositions and flow rate while achieving desired product specification. The project team found technical approaches and process designs for application of the process to gas fields with flow rates varying from 0.05 to 10 MMscfd and nitrogen contents

ranging from 6 to 60%. “Dial-in” capabilities were developed that allow customers to vary flow rates and nitrogen content of gas fed to the membrane skid “on the fly.”

New, larger twelve-inch diameter gas separation membrane modules were used for the first time during this project. Their successful introduction will allow significant cost reductions on a per-square meter-of-membrane basis for any membrane applications requiring high feed flow rates.

During early commercialization, MTR discovered an important potential future market for the NitroSep™ technology: bringing very-high-nitrogen-content gas streams containing as much as 40-50% nitrogen down to levels of 10-15%. This market differs from the initial target of bringing all product streams to 2-4% nitrogen. Many gas producers operate with access to large gas gathering and processing networks. For this type of operator, bringing the nitrogen content of high-nitrogen wells to the 10-15% level allows them to use the resulting product stream for blending with larger volume low-nitrogen content streams. In some ways, this was a good news/bad news result. The good news was finding the new market, the bad news was recognizing that dilution is hard to compete against in the entire nitrogen/natural gas separation market. Fortunately for membrane companies, nitrogen is difficult to economically separate from methane by any technology. This means membrane systems are the lowest cost way to treat many types of nitrogen-containing gas streams, when treatment is required.

MTR believes the NitroSep™ membrane process solution fulfills the various needs of natural gas producers for wellhead nitrogen/methane separation. The MTR membrane process can provide

- mobile units
- adaptability to varied and transient feed gas conditions
- lower installation and maintenance costs than competing technologies
- simplicity of design
- automatic unmanned operation

MTR’s membrane process provides significant economic benefits of recovering previously shut-in or flared natural gas, and also greatly reduces on-site methane emissions to the air. This provides attractive benefits not only for gas producers, but for the environment as well.

The improved customer confidence gained during this project may turn out to be one of the most important contributions to future success of this technology. Moving from the small sub-1 MMscfd units developed early in the project to the 10-100 MMscfd size of current and future units is giving more confidence to gas industry participants that high-nitrogen-content sources or explorations can be economically monetized instead of being passed over or disregarded. The technology has matured over the course of the project, and is now fully prepared to be commercially deployed.

6. REFERENCES

1. R.W. Baker, *Membrane Technology and Applications*, 2nd edition, John Wiley & Sons, Ltd., Chichester, UK (2004).
2. K.A. Lokhandwala, A.R. Da Costa, M. Jacobs, and R.W. Baker, "Membrane Systems for Nitrogen Rejection," *81st Annual Gas Processors Association (GPA) Convention*, Dallas, TX (March 11-13, 2002).
3. P. Hale, Randall Gas Technologies-ABB Lummus Global Inc, and K. Lokhandwala, Membrane Technology and Research, Inc., "Advances in Membrane Materials Provide New Solutions in the Gas Business," presentation at *Laurance Reid Gas Conditioning Conference (LRGCC)*, University of Oklahoma, Norman, OK, February 27-March 3, 2004.
4. P. Hale, Randall Gas Technologies-ABB Lummus Global Inc, and K. Lokhandwala, Membrane Technology and Research, Inc., "Advances in Membrane Materials Provide New Solutions in the Gas Business," presentation at *83rd GPA Annual Meeting*, New Orleans, LA, March 13-16, 2004.
5. A. Jariwala and K. Lokhandwala, "Nitrogen-Rejecting Membranes To Increase Gas Heating Value And Recover Pipeline Natural Gas: A Simple Wellhead Process Approach," *12th Annual International Petroleum Environmental Conference*, Houston, TX, November 8-11, 2005.
6. K. Lokhandwala and A. Zammerilli, "New Nitrogen-rejection Membrane Technology Commercialized," *GasTIPS 12 (4)*, 16-19 (2006).
7. K. Lokhandwala and R. W. Baker, "Natural Gas Processing with Membranes: An Overview," submitted to *I&EC Fundamentals*, Summer 2007.

Website references:

www.netl.doe.gov/technologies/oilgas/NaturalGas/Projects_n/EP/NGProcessing/NGP_4122_5DemoSeparateNitrogen.html

<http://www.mtrinc.com/Pages/NaturalGas/ng.html>

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